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MELT VISCOSITY : PART II

Esters and Acetyl Derivatives of Shellac and its Constituents

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ABSTRACT. The results of viscosity measurements of esters and acetyl derivatives of shellac resins have shown that both hydroxyl and carboxyl groups exert their influence in micelle formation of the individual resins, but the influence which soft resin exerts on the micelle formation of hard resin in shellac is mainly due to its hydroxyl group.

INTRODUCTION

As reported in a previous communication (Basu, 1947) the results of viscosity measurements on molten shellac resins have shown that the resin molecules are greatly aggregated owing to the presence of a large number of active polar groups in them. In the present paper an attempt has been made to find out the role of the various functional groups, namely, hydroxyl and carboxyl groups in "micelle" formation. This end has been achieved by protecting the polar groups by esterification and acetylation, and examining their effect on the energy of activation and viscous volume.

EXPERIMENTAL

Apparatus.—The viscometer used was the same as described in a previous paper (Basu, *loc. cit.*) and the same procedure was adopted in calculating the values of activation energy and viscous volume.

Preparation : Acetyl derivative.—Acetyl derivatives were prepared in each case by refluxing the weighed quantity of powdered resin with a mixture of 1 : 3 acetic anhydride : pyridine mixture (5 c.c. of mixture per gramme of substance) for 2-3 hours. The resulting solution was poured into water, and the precipitated resin thoroughly washed, and dissolved in a 1 : 1 benzene-alcohol mixture. The last trace of acid was removed by neutralising the benzene-alcohol solution with solid bicarbonate. The solution thus neutralised was poured into water, washed thoroughly and then dried at 50°C in vacuum. The product thus obtained corresponded to 6.83 acetylated derivative for hard resin, 4.79 acetylated derivative for shellac and 1 acetylated derivative for soft resin. Use of hot water should be avoided since this leads to decomposition of the acetylated products especially in the case of hard resin and shellac.

Ethyl ester.—20% ethyl alcoholic solution of the dried sample was saturated with dry hydrochloric acid gas, left overnight and then refluxed for

2-3 hours. The resulting solution was cooled, neutralised with bicarbonate and then poured into water. The precipitated resin was repeatedly washed with distilled water and then dried in vacuum at 60°C. The acid value for soft resin ester was zero, but in the case of shellac and hard resin it varied from 3 to 5.

The separation of hard and soft resin was effected by ether extraction method.

RESULTS

The results of viscosity determination of acetyl derivatives of shellac, hard resin and soft resin are summarised in Tables I-VI and the corresponding curves given in Figs. 1-3.

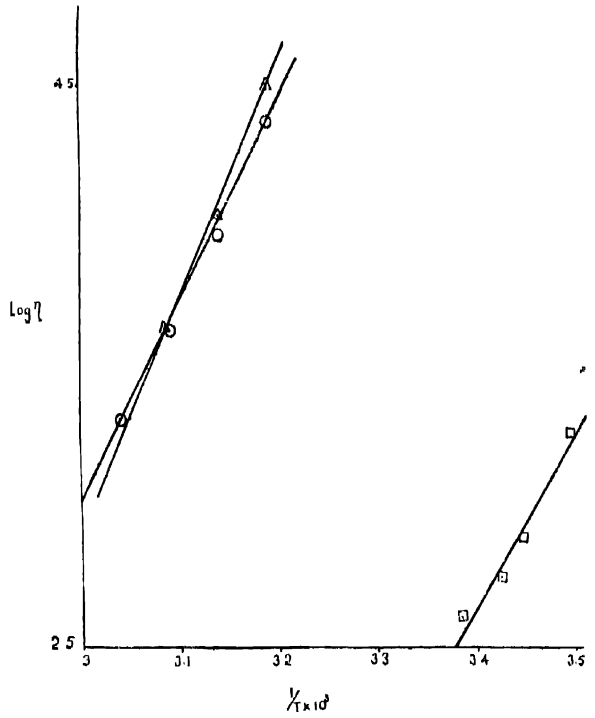

FIG. 1

Acetyl derivative

⊙ hellac △ Hard Resin □ Soft Resin

ACETYL DERIVATIVES

TABLE I

Shellac

$f = 5.495 \times 10^3$ dynes/cm²

$1/T \times 10^{-3}$	η (pois)	log η
3.09	4340.25	3.6375
3.14	1,0448.75	4.0190
3.19	3,3339.55	4.5229

TABLE II

Hard Resin

$f = 5.495 \times 10^3$ dynes/cm²

$1/T \times 10^{-3}$	η (pois)	log η
3.04	2057.60	3.3133
3.09	4404.55	3.6440
3.14	9259.20	3.9665
3 19	2,3437.35	4.3699

TABLE III

Soft Resin

$f = 5.495 \times 10^3$ dynes/cm²

$1/T \times 10^{-3}$	η (pois)	log η
3.508	1832.55	3.2629
3.448	771.60	2.8874
3.424	546.55	2.7376
3.389	417.95	2.6210

TABLE IV

Shellac

T°K = 323

f(dynes/cm²)	η (pois)	log η/f
11.988×10^3	2186.2	−0.7391
20.149×10^3	1350.3	−1.1480
25.475×10^3	964.5	−1.4219
30.969×10^3	710.3	−1.0397

TABLE V

Hard Resin

T°K = 321

f(dynes/cm²)	η (pois)	log η/f
11.988×10^3	5465.50	−0.3412
21.711×10^3	2893.50	−0.8391
25.475×10^3	2250.50	−1.0538
28.472×10^3	1961.15	−1.1619

TABLE VI

Soft Resin

T°K = 284

f(dynes/cm²)	η (pois)	log η/f
5.495×10^3	2025.45	−0.4335
8.492×10^3	1286.00	−0.8198
10.489×10^3	1093.10	−0.9820
12.488×10^3	868.05	−1.1580

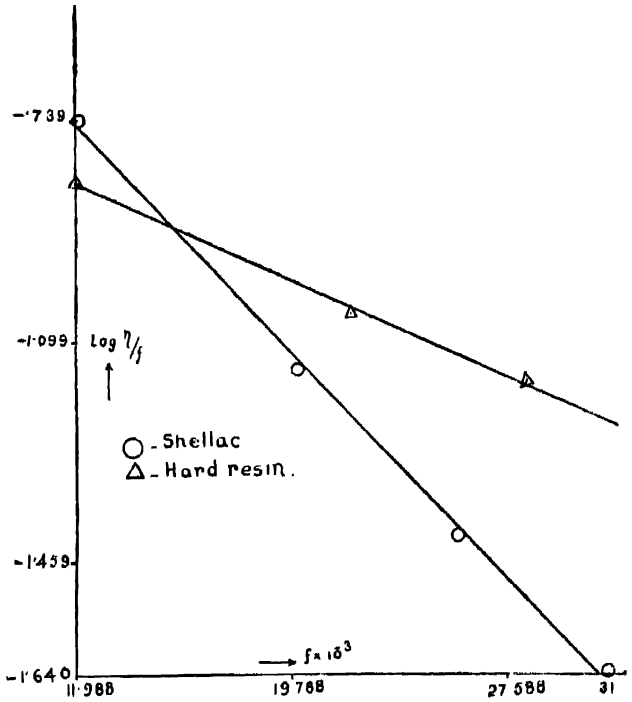

FIG. 2

Acetyl derivative

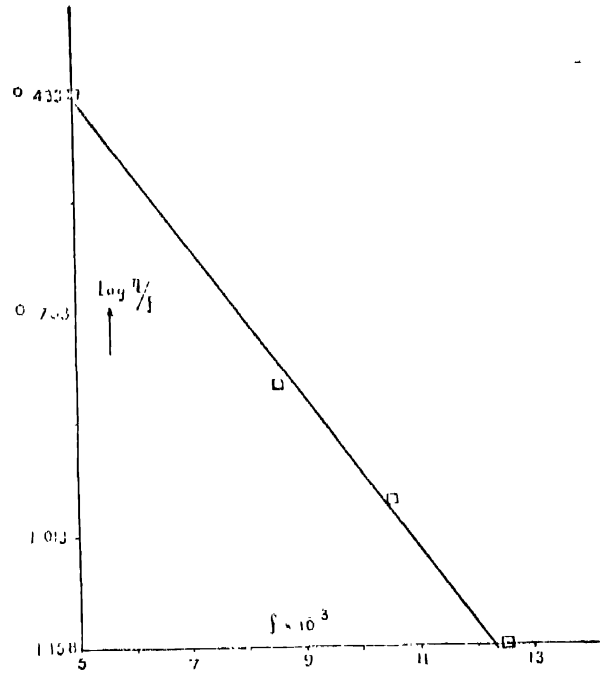

FIG. 3
Acetyl derivative. Soft Resin

Similar results for esters are given in Tables VII-XII and the corresponding log η-1/T and log η/f-f curves are given in Figs. 4-5.

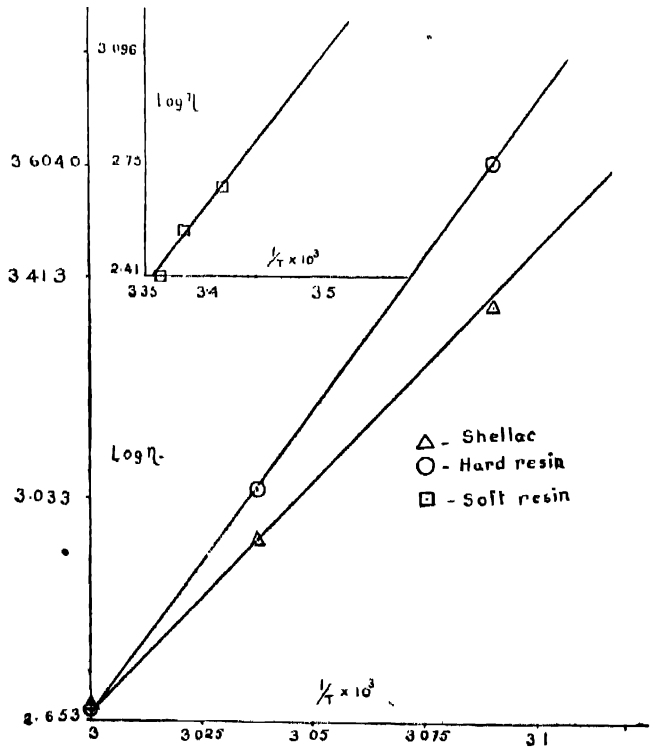

FIG. 4
Ethyl Ester

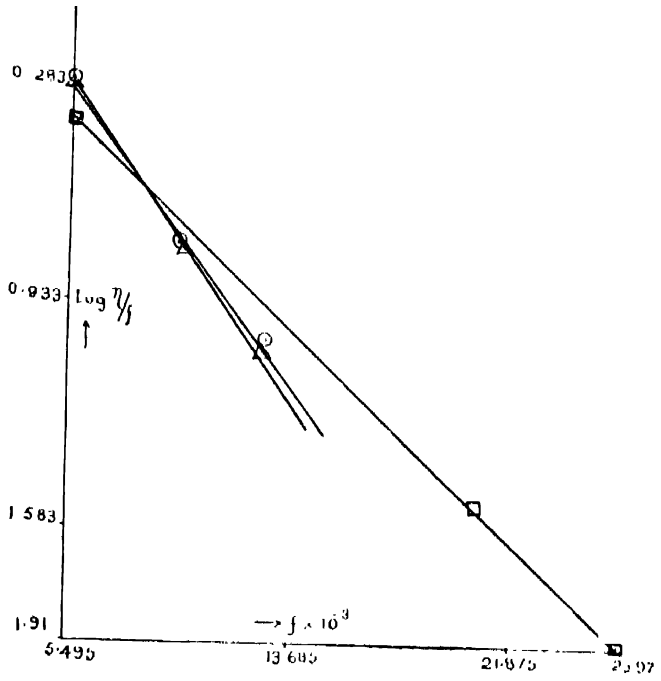

FIG. 5

Ethyl Ester

⊙ Hard Resin △ Soft Resin □ Shellac

ETHYL ESTERS

TABLE VII

Shellac

$f = 5.495 \times 10^3$ dynes/cm²

$1/T \times 10^{-3}$	η (in pois)	log η
3.09	2057 60	3 3133
3.04	932 35	2 0696
3.00	450.10	2 6532

TABLE VIII

Hard Resin

$f = 5.495 \times 10^3$ dynes/cm²

$1/T \times 10^{-3}$	η (in pois)	log η
3 09	2535 00	3.4040
3 04	1093 10	3 0386
3.00	450 15	2.6533

TABLE IX

Soft Resin

$f = 5\ 495 \times 10^3$ dynes/cm²

$1/T \times 10^{-3}$	η (in pois)	log η
3.546	2797 05	3 4467
3 424	546.55	2 7376
3.389	353.65	2.5487
3.367	257 20	2.4102

TABLE X

Shellac

T°K = 323

f (dynes/cm²)	η (pois)	log η/f
5.495×10^3	2057.60	−0 4267
12.488×10^3	932.35	−1.1270
20.979×10^3	417.95	−1.7017
25.974×10^3	321.50	−1 9073

TABLE XI

Hard Resin

T°K = 325

f (dynes/cm^2)	η (pois)	log η/f
5.4950×10^3	2862.2	−0.2833
9.4910×10^3	1546.2	−0.7881
12.4875×10^3	1157.4	−1.0329

TABLE XII

Soft Resin

T°K = 282

f (dynes/cm^2)	η (pois)	log η/f
5.495×10^3	2797.05	−0.2933
9.491×10^3	1511.05	−0.7980
12.488×10^3	1125.25	−1.0450

The values of a, b, E_0' and $\lambda\lambda_2\lambda_3$ for esters and acetyl derivatives as obtained from the above Tables and the corresponding graphs are given in Tables XIII and XIV.

TABLE XIII

Acetyl Derivatives

	a	b	E_0' (K-cal)	$\lambda\lambda_2\lambda_3$ (in cc.)
Hard resin ...	1.6403×10^4	2.443×10^{-2}	31.81	10.154×10^{-18}
Shellac ..	1.3714×10^4	3.694×10^{-2}	28.74	10.292×10^{-18}
Soft resin ...	1.2782×10^4	6.767×10^{-2}	25.32	18.622×10^{-18}

TABLE XIV

Ethyl Esters

Hard resin ...	1.8100×10^4	8.013×10^{-2}	35.94	22.07×10^{-18}
Shellac ...	1.5086×10^4	6.117×10^{-2}	29.89	16.83×10^{-18}
Soft resin ...	1.3606×10^4	4.944×10^{-2}	27.08	13.61×10^{-18}

DISCUSSION

A glance at Tables XIII and XIV will show that on protecting the polar groups the activation energy for viscous flow is greatly reduced. In the case of esters, this is evidently due to the difference in cohesive forces between ester groups and carboxyl groups. Mark and Meyer (1930) have shown that cohesive forces in K-cal/mole for carboxyl and ester groups are respectively 8.97 and 5.60. Hence the lower value of cohesive force between ester groups is responsible for the lower activation energy, *i.e.*, lower degree of association of shellac esters.

An anomalous case is presented by the acetyl derivatives. The cohesive force between acetyl groups is not actually so low as (Mark and Meyer, *loc. cit.*) to cause such a great reduction in the activation energy of the acetylated products. But since the acetyl group is much bulkier than the hydroxyl group and cannot therefore fit in tightly in the original micelle of shellac, the

whole structure becomes extended, easily deformable and less aggregated owing to the greater average distance through which the cohesive forces have now to operate.

Another interesting observation that can be made from the values of activation energy and viscous volume for acetyl derivatives is that these values for shellac in every case are nearly the weighted averages of those of hard and soft resin. Thus we may assume that the effect which soft resin exerts on hard resin in micelle formation is mainly due to its own hydroxyl groups interacting with those of the hard resin. Naturally we may assume that aggregation is mainly due to attraction between the hydroxyl groups, *i.e.*, the OH groups are responsible for intramiceller forces, while the intermiceller forces are due to COOH groups. If these assumptions be true then the difference between the activation energy for pure resin and that of its ester will be equal to the difference between the same quantities for carboxyl groups and ester groups. Taking, for example, the case of soft resin, the difference between the activation energy for soft resin and that of its ester is 6.35 K-cal/mole, while that between esters and carboxyl groups is 3.3 K-cal/mole. The difference is too high to be ascribed to experimental error. Thus we can conclude that both hydroxyl and carboxyl groups exert their influence in micelle formation of individual resins but it is the hydroxyl group which is responsible for mutual interaction of resins.

The interpretation of the values for viscous volume as obtained for esters and acetyl derivatives is difficult. Since esterification and acetylation cause some strong polar attraction to vanish from the molecule, the molecules get an entirely new orientation in the micelle and the same idea as expressed in the previous communication as regards the jumping of the micelle between polar groups, cannot be applied here.

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REFERENCES

Basu, S., 1947, *Ind. J. Phys.*, **21**, 7.

Mark and Meyer, 1930, Der Aufbau der Hochpolymeren Organischen Naturstoffe, Leipzig, p. 27.